

TITLE OF INVENTION

Fluoropolymer Yarn Blends

BACKGROUND OF THE INVENTION

1. Field of the Invention.
5 This invention relates to blends of fluoropolymer yarn with other yarns.
2. Description of Related Art.
U.S. Patent Publication 2002/0079610 A1 discloses the melt spinning of fluoropolymer yarn at a high temperature above the melting point of the fluoropolymer to produce high tenacity yarns at high rates of production relative to prior fluoropolymer yarns and processes. The addition of colorant to the fluoropolymer prior to yarn formation is disclosed, i.e., the pigment is added to the copolymer prior to melt spinning so that the melt spun yarn has the color of the pigment,
15 depending on the pigment concentration. The reason the colorant (pigment) is added to the fluoropolymer prior to melt spinning is that the chemical inertness of the fluoropolymer yarn makes it virtually undyeable by conventional textile fiber dyeing processes and dyes after spinning. Dyeing has the advantage over pigment coloring by offering greater
20 versatility in enabling the conversion of an undyed yarn to a wide range of colors. Fluoropolymer yarn has not provided this versatility. Thus, without pigment coloring, the fluoropolymer exhibits a natural color, which ranges from white to milky white (translucent), to transparent. Another problem with fluoropolymer yarns is that they do not have the strength of common
25 high tenacity synthetic textile fiber yarns, i.e., polyester and polyamide, usually greater than 5.9 gpd (g/den). As disclosed in Example 9 of the above-identified Patent Publication, PFA polymer (tetrafluoroethylene/perfluoro(propyl vinyl ether) copolymer is melt spun at different rates to produce yarn having a tenacity/elongation of 0.94-1.10 gpd/68-80%
30 elongation and 1.41 gpd/25% elongation, revealing the usual situation of elongation decreasing as tenacity increases. The highest tenacity yarn prepared in the Patent Publication is disclosed in Example 26, wherein the ethylene/tetrafluoroethylene copolymer yarn has a tenacity of 2.44 gpd and elongation of 18.8%.

35 BRIEF SUMMARY OF THE INVENTION

One aspect of the present invention solves the problem of providing color to fluoropolymer which has no added color, i.e., it is neither pigmented nor dyed, the latter because the fluoropolymer is undyeable by

conventional textile fiber dyes and dyeing processes. The embodiment solving this problem can be described as a yarn blend of at least first and second yarns, said first yarn comprising fluoropolymer fiber and said second yarn comprising at least one dyed or dyeable fiber comprising

5 polyester, polyamide, or acrylic. Although the first and second yarns can be combined into the yarn blend by twisting together, the preferred method of combining the yarns is by co-mingling by an air jet blending process. The second yarn can be undyed at the time of combining with the first yarn, followed by subjecting the yarn blend to dyeing, which colors only

10 the second yarn. Alternatively, the second yarn can be dyed prior to combining with the first yarn. In either embodiment, the yarn blend has the appearance of the color of the second yarn, with the color being the most uniform when the combining of the yarns is by co-mingling. The weather resistance (chemical stability, dampness, sunlight, high and low

15 temperature exposure) of the fluoropolymer yarn component of the yarn blend makes it especially useful in outdoor applications. A particularly preferred application is sewing thread comprising multiple ends of the yarn blend to achieve the breaking strength desired. Sewing threads are available in a wide variety of colors to match the variety of colored fabrics

20 that are available. The sewing thread of the present invention has the versatility of being dyeable in these wide variety of colors, by virtue of the dyeability of the polyester, polyamide, and/or acrylic fiber making up the second yarn. A preferred sewing thread of the present invention includes a binder. Binders for the second yarn do not normally adhere to

25 fluoropolymer, because of the well-known non-stick property of fluoropolymers. Surprisingly, application of the binder to the yarn blend serves to bind both the fluoropolymer and the second yarn together, so that the resultant bound sewing thread can provide the most trouble-free (snag free) sewing by using conventional industrial sewing equipment.

30 Another aspect of the present invention solves the problem of the tenacity of the fluoropolymer yarn by itself having less than desired tenacity for certain applications. This problem is solved by the yarn blend of first and second yarns described above wherein the elongation and tenacity of said second yarn is such that the overall tenacity of said yarn

35 blend is at least 1 gpd greater than the first yarn by itself. Polyester and polyamide yarns typically have high elongation, such that the second yarn merely being stronger than the first yarn does not give a stronger yarn blend if the second yarn merely elongates under the tension applied to the

yarn blend while the elongation of the first yarn is exceeded, resulting in breakage of the first yarn. Thus, it is preferred that the elongation of the second yarn should be no greater than the elongation of the first yarn. This is difficult to achieve, however, because high tenacity second yarns 5 have high elongation, e.g., greater than 20, while high tenacity first yarns typically have lower elongations, e.g., less than 15%. Surprisingly, it has been discovered that even though the second yarn has a higher elongation than the first yarn, the second yarn can still increase the tenacity of the yarn blend. Preferably, the elongation of the second yarn is 10 less than 10% above that of the first yarn, i.e., if the first yarn has an elongation of 10%, the elongation of the second yarn should be less than 20%.

It is preferred that the fluoropolymer yarn is as strong as possible, so that in outdoor utility as the strength of the second yarn diminishes from 15 weathering, the first yarn component of the yarn blend provides sufficient residual strength required for the particular application. Thus, it is preferred that the first yarn in the yarn blend has a tenacity of at least 2 gpd and the tenacity of said second yarn is at least 5.9 gpd, with the second yarn having an elongation as described in the preceding 20 paragraph. Typically the tenacity of the first yarn will not exceed 5 gpd.

Surprisingly, it has been found that the presence of the fluoropolymer yarn in the yarn blend increases the weatherability of the second yarn, such that the higher tenacity of the yarn blend arising from the presence of the second yarn when it is polyester or polyamide is 25 surprisingly high in view of the deterioration of the tenacity of the second yarn when exposed by itself to the same weathering.

DETAILED DESCRIPTION OF THE INVENTION

To first describe the yarns making up the yarn blend of the present invention, examples of fluoropolymer from which the first yarn can be 30 made include the following: (A) non-melt-fabricable polytetrafluoroethylene, including modified polytetrafluoroethylene, i.e., wherein a small amount of comonomer is copolymerized with the tetrafluoroethylene and (B) melt-fabricable fluoropolymers, including homopolymers other than polytetrafluoroethylene (PTFE), such as 35 polyvinylidene fluoride (PVDF), and perfluorinated copolymers, such as copolymers of tetrafluoroethylene (TFE) prepared with comonomers including perfluoroolefins and perfluoro(alkyl vinyl ethers)(PAVE), wherein the alkyl group contains 1 to 6 carbon atoms and the PAVE can be more

than one PAVE, or blends of such polymers. The term "copolymer", for purposes of this invention, is intended to encompass polymers comprising two or more comonomers in a single polymer. A representative perfluoroolefin is hexafluoropropylene. Representative perfluoro(alkyl vinyl ethers) are perfluoro(methyl vinyl ether) (PMVE), perfluoro(ethyl vinyl ether) (PEVE), and perfluoro(propyl vinyl ether) (PPVE). Preferred highly fluorinated polymers are the copolymers prepared from tetrafluoroethylene and one or more perfluoro(alkyl vinyl ethers) and the copolymers prepared from tetrafluoroethylene and hexafluoropropylene. Most preferred

5 copolymers are TFE with 1-20 mol% of a perfluoroolefin comonomer, preferably 3-10 mol% hexafluoropropylene or 3-10 mol%

10 hexafluoropropylene and 0.2-2 mol% PEVE or PPVE, commonly known as FEP, and copolymers of TFE with 0.5-10 mol% perfluoro(alkyl vinyl ether), including 0.5-3 mol% PPVE or PEVE, commonly known as PFA, or such

15 copolymers which contain both PMVE and one or more of PEVE and PPVE, commonly known as MFA. The fluoropolymers (B) described above preferably exhibit a melt flow rate (MFR) of 1 to about 50 g/10 minutes as determined at 372°C according to ASTM D2116, D3307, D1238, or corresponding tests available for other highly fluorinated

20 thermoplastic polymers. Polyvinylidene fluoride preferably has a melt viscosity of 1 to 4×10^3 Pa•s measured in accordance with ASTM D 3222.

In addition to the fluorinated thermoplastic tetrafluoroethylene copolymers (B) described above, such fluorinated thermoplastic (melt-fabricable) polymers as ethylene/tetrafluoroethylene copolymers (ETFE)

25 and ethylene/chlorotrifluoroethylene (ECTFE) can also be used in the present invention, with ETFE being preferred. Such ETFE is a copolymer of ethylene and tetrafluoroethylene, preferably containing minor proportions of one or more additional monomers to improve the copolymer properties, such as stress crack resistance. U.S. Patent 3,624,250

30 discloses such polymers. The molar ratio of E (ethylene) to TFE (tetrafluoroethylene) is from about 40:60 to about 60:40, preferably about 45:55 to about 55:45. The copolymer also preferably contains about 0.1 to about 10 mole % of at least one copolymerizable vinyl monomer that provides a side chain containing at least 2 carbon atoms. Perfluoroalkyl

35 ethylene is such a vinyl monomer, perfluorobutyl ethylene being a preferred monomer. The polymer has a melting point of from about 250°C to about 270°C, preferably about 255°C to about 270°C. Melting point is determined according to the procedure of ASTM 3159. In accordance with

this ASTM procedure, the melting point is the peak of the endotherm obtained from the thermal analyzer. Preferably, the ETFE used in the present invention has a melt flow rate (MFR) of less than 45 g/10 min using a 5 kg load in accordance with ASTM D 3159, wherein the melt 5 temperature of 297°C is specified. More preferably, the MFR of the ETFE is no more than 35 g/10 min and is at least 15 g/10 min, preferably at least 20 g/10 min. As the MFR increases from 35 g/10 min, resulting from 10 reduced molecular weight of the polymer, the advantage of higher in melt spin rate becomes counterbalanced by reduced strength (tenacity) of the yarn from the reduced molecular weight polymer, such that upon reaching an MFR of 45 g/10 min, the decrease in tenacity outweighs the increase in production rate. As the MFR decreases from 20 g/10 min, the difficulty in 15 extruding the more viscous polymer increases, leading to uneconomical melt spin rates, until an MFR of 15 g/10 min is reached, below which the polymer is barely melt spinnable through the small extrusion orifices required for yarn.

Also suitable for the practice of this invention are blends of the highly fluorinated thermoplastic polymers including blends of TFE copolymers.

20 The fluoropolymers (A) can be formed into yarn by known processes, including spinning of the fluoropolymer into the yarn or forming sheets or strands of the fluoropolymer, followed by cutting filaments therefrom. The fluoropolymers (B) can be melt spun into yarn preferably by the process disclosed in U.S. Patent Publication 2002/0079610 A1. 25 The ETFE copolymer yarns can have a tenacity of at least 2 gpd and preferably at least 2.5 gpd. A preferred process to make a yarn having a tenacity of at least 3 gpd is described in the Examples hereinafter. Typically, the fluoropolymer yarn used to make yarn blends of the present invention will have an elongation of 8 to 25% and preferably from 8 to 15% 30 to provide the higher tenacities.

Yarn deniers disclosed herein are determined in accordance with the procedure of ASTM D 1577 and the tensile properties (elongation to break (elongation) and tenacity) are determined in accordance with the procedures disclosed in ASTM 2256.

35 Yarns of polyester, polyamide, acrylic polymer are commercially available and can be used as second yarns to make yarn blends of the present invention. Such yarns and processes for making them and processes for dyeing them are disclosed in Kirk-Othmer, Encyclopedia of

Chemical Technology, 4th Ed, (1994) in Vol. 10, pp. 559-565 and 576-581 (acrylics) and pp. 662-667, 670-677 (polyesters), and in Vol. 19, pp. 519-522, 528, 530-539, and 543-544 (polyamides). Polyester and polyamide yarns are made by melt spinning, while polyacrylic yarns are typically 5 made by wet or dry spinning. The polyesters, polyamides, and acrylic polymers used to make the yarns can be homopolymers or copolymers and have sufficiently high molecular weight to provide the tenacity desired for the yarn blend of the present invention. Suitable homo- and/or copolymers which may be used include for example, poly(ethylene 10 terephthalate), poly(propylene terephthalate), poly[ethylene terephthalate/(5-sodium sulfo)isophthalate]. Polyhexamethylene adipamide, polyhexamethylene adipamide containing sulfo or amino groups receptive to cationic or dark acid dyes respectively and the like and mixtures thereof. Examples of acrylic polymers include: acrylonitrile 15 homopolymer and copolymers, including the modacrylics, i.e., acrylonitrile copolymers containing 35 to 85 wt% acrylonitrile units.

The tenacity of the second yarn will depend on the polymer from which it is made and the degree of draw to increase tenacity once the yarn is formed. The tenacity will also depend on whether the second yarn is 20 continuous filament or staple fiber. For a given polymer, the continuous filament yarn has a higher tenacity than a staple fiber yarn. To solve the problem of providing a colored yarn, which contains uncolored fluoropolymer yarn, the tenacity of the second yarn is less important. Thus, acrylic polymer yarn, which is only available as staple fiber yarn and 25 has a tenacity of 2 to 3 gpd, can be used. Polyester staple fiber yarns generally exhibit tenacities of 2.4 to 7 gpd, and polyamide staple fiber yarns exhibit tenacities of 2.9 to 7.2 gpd. At the higher tenacity levels however, even for the acrylic polymer yarn, the staple fiber yarn can provide a yarn blend with the fluoropolymer yarn that exhibits a greater 30 tenacity than the fluoropolymer yarn by itself. The same is true for continuous filament polyester and polyamide yarns in general, which exhibit a tenacity of at least 3.5 gpd. To provide a yarn blend having a greater tenacity than the fluoropolymer yarn component, however, the use of high tenacity polyester and polyamide yarn as second yarns is 35 preferred. Such yarns exhibit tenacities of at least 5.9 gpd, and preferably at least 6.5 gpd. Generally the tenacity of the polyester and polyamide yarns will not exceed 9 gpd.

- Typically, the second yarn will have an elongation of 15 to 30%. Preferably, the elongation of the second yarn is less than 8% above that of the first yarn, more preferably less than 5% above that of the first yarn, and most preferably less than 2 % above that of the first yarn. These
- 5 differences in elongations apply to each of the first and second yarns described herein. It is also preferred that the first yarn in the yarn blend has a tenacity of at least at least 2.5 gpd and more preferably at least 3 gpd. It is also preferred that the tenacity of the second yarn be at least 2 gpd greater than the tenacity of the first yarn.
- 10 The first yarn of the present invention can be monofilament or multifilament. When the yarn is a monofilament, it will generally have a diameter of 50 to 1000 micrometers. When the yarn is multifilament, the individual filaments will generally have a diameter of 8 to 30 micrometers, and the yarn will generally have a denier of 30 to 5000, preferably 100-1000 and contain 20 to 200 filaments. In the case of the multifilament yarn, the individual filaments will preferably each be 2 to 50 den, preferably 5 to 40 den/filament, and most preferably 10-30 den/filament, with 20-30 den/filament being preferred for highest breaking strength without undue stiffness. The second yarn will preferably be a
- 15 multifilament yarn that can be characterized by the same parameters characterizing the multifilament first yarn earlier in this paragraph. The first and second yarns can also be made of staple fiber rather than continuous filament to enhance appearance, and the yarn blend of the present invention can be a mixture of continuous filament and staple fiber
- 20 yarns. In the case of staple fiber first and/or second yarns used in the yarn blend of the present invention, the staple fibers will generally have a denier of 1-10, preferably 1 to 5 den/fiber (or filament from which the fiber is made).
- 25 The first and second yarns can be blended by conventional textile fiber processes, such as twisting, and pairs of twisted blend yarns can be further twisted together e.g., in the opposite twist direction to form cords. The yarns can be as spun, i.e., flat yarn, or textured by conventional processes to increase the bulk of the yarn. Dyeing of the second yarn either before or after forming the yarn blend will impart the second yarn color to the color of the yarn blend, to twisted pairs of the yarn blend and to cord of the yarn blend, even though the first yarn is undyed.
- 30 A preferred process for blending the first and second yarns together is co-mingling such as described in "Air-Jet Texturing & Mingling",

published by Loughborough University (1989) as a collection of papers presented at an international conference at the University in September 1989, which includes the paper presented by A. Demic, "Intermingling/Interlacing: A Broad Survey (pp.41-60). Intermingling is

5 described as subjecting a loose bundle of flat or textured yarn to turbulent cold air-jet impingement (mingling jet) at an angle to the path of the yarn to open up sections of the filaments, while in the vicinity of the opened up section of the filaments, the filaments become intertwined and intermingled with each other to form compact sections. Co-mingling is

10 described as carrying out the intermingling process on two yarns, whereby the intertwining and intermingling involves filaments of both yarns. The resultant co-mingled yarn is a coherent yarn, i.e., the two yarns are united into a single yarn (blend), and the resultant yarn blend is in the form of interlaced sections periodically alternating with open sections. This

15 description and method of preparation applies to the co-mingled yarn blend of the present invention. The co-mingled yarn blend of the present invention resembles the yarn blend depicted as "Blending" in Fig. 5 on p. 59 of the Demic paper. The air jets used for co-mingling and the conditions for carrying out the co-mingling process are well known, such

20 as described in the Demic paper and disclosed as intermingling in U.S. Patent 4,025,595. When the yarn fed to the co-mingling jet is textured, the texturing can include different types of texturing such as air-jet texturing, false twist texturing, and hot-fluid texturing. The co-mingled yarn blends of the present invention preferably have 3 to 50 entanglements per meter

25 (determined as disclosed in col. 3 of U.S. Patent 4,025,595) to achieve the coherence desired for textile processing. The entanglements along the length of the blended yarn are knots, the knots sometimes being called nips or nodes, and these entanglements provide integrity to the blended yarn. Even when the first yarn is monofilament or staple fiber, the second

30 yarn filaments will interlace with the monofilament or staple fiber yarn to provide a blended yarn having integrity. The same is true when one or both of the yarns are staple fiber yarns. In a preferred yarn blend, both the first and second yarns are multifilament yarns, which provides the highest tenacities for the yarn blend and also the most uniform color appearance

35 of the yarn blend, this being the dyed color of the second yarn.

Another preferred yarn blend of the present invention is the yarn blend comprising a core and a sheath, with the second yarn being present in the core and the first yarn being present in the sheath. This yarn blend

can be made by wrapping the first yarn around the second yarn, but is preferably made by co-mingling, wherein the first yarn is overfed to the co-mingling jet relative to the feed of the second yarn to the jet, tending to cause filaments of the first yarn to wrap around the second yarn while the 5 filaments of each yarn become interlaced together by the co-mingling process. The over feed of the first yarn is achieved by feeding the first yarn to the co-mingling jet at a faster rate than the windup of the yarn blend downstream from the jet. This construction of the yarn blend of the present invention has the advantage of better utilization of the greater 10 strength of the second yarn to increase the strength of the yarn blend over the strength of the first yarn. The nature of the sheath yarn, i.e., the first yarn, in this construction is not a complete covering of the core yarn, i.e., the second yarn, whereby the dyed color of the second yarn nevertheless provides coloration of the yarn blend. The first yarn contributes to the yarn 15 blend color by picking up the color of the second yarn, some by reflectance and some by light transmission so that the second yarn color is visible through the thickness of the filaments of the first yarn.

One criterion for combining the first and second yarns into yarn blends of the present invention is the denier desired for the yarn blend. 20 Such denier is achieved by selection of the denier of the first and second yarns and by the number of each such yarns in the yarn blend. The yarn blend can consist of an equal number of first and second yarns. Alternatively, the number of first yarns can exceed the number of the second yarn or vice versa. A preferred yarn blend has two first yarns and 25 one second yarn, and another preferred blend has two second yarns and one first yarn. The first mentioned preferred yarn blend maximizes the fluoropolymer yarn content for maximum residual outdoor weathering strength. The second-mentioned preferred yarn maximizes initial yarn blend strength and color uniformity. These objectives can also be achieved by the relative denier of the first and second yarns. For example, a higher denier second yarn tends towards maximizing color 30 uniformity and high initial yarn blend strength when only one second yarn is present, depending the denier difference between first and second yarns. In the case of co-mingled yarn blends of the present invention, when one or both of the first and second yarns are staple fiber yarns, a plurality of staple fiber yarns is preferably used so as to increase the 35 opportunity for intermingling between yarns and between staple fibers in each yarn.

The second yarn can be dyed by conventional textile fiber dyeing processes and using conventional textile fiber dyes, depending on whether the second yarn is made of polyester, polyamide, or acrylic fiber. Further description of such dyeing processes and dyes and modifying the polymer

- 5 making up the yarn is disclosed in Kirk-Othmer referred to above. The second yarn can be dyed before after combination into the yarn bend.
Dyeing of the yarn blend leaves the first yarn undyed.

A preferred yarn blend contains at least two second yarns, one of which is acrylic staple fiber and the other of which is either polyester or
10 polyamide or both. Such yarn blend is especially useful in applications exposed to the weather, wherein the dye fastness of the acrylic fiber maintains color for the yarn blend, while the fluoropolymer yarn provides long-term strength.

EXAMPLES

15 The yarn used in the Examples is Tefzel® ETFE fluoropolymer which is a terpolymer of ethylene, tetrafluoroethylene, and less than 5 mole% perfluoroalkyl ethylene termonomer, having a melting temperature (peak) of 258°C and melt flow rate of 29.6 g/10 min, both as determined in accordance with ASTM 3159, using a 5 kg weight for the MFR
20 determination.

The lubricant used to coat the yarn after melt spinning is as follows:
88.9 wt% Clariant Afilan® PP polyol polyester, 5 wt% Uniqema® G-1144 polyol ethoxylated capped ester oil emulsifier, 0.67 wt% Cytek Aerosol® OT di-octyl sulfosuccinate wetting agent (75 wt% aqueous solution), 5 wt%
25 Cognis Emersol 871 fatty acid surfactant, 0.26 wt% Uniroyal Naugard® PHR phosphite antioxidant, 0.67 wt% sodium hydroxide (45 wt% aqueous solution) stabilizer for the fatty acid, and 0.04 wt% Dow Corning polydimethylsiloxane (process aid – minimizes deposits of the lubricant on the hot rolls).

30 The fluoropolymer and the lubricant have surface tensions of 25 dynes/cm and 23.5 dynes/cm respectively, at ambient temperature.

The melt spinning of the fluoropolymer is carried out using an equipment arrangement as shown in Fig. 9 of U.S. Patent Publication 2002/0079610 A1, except that the kiss roll 112 and the guides 111 are not present, and the lubricant is applied using an applicator guide positioned beneath the annealer 110, upstream from the change in direction guide. The application guide is similar to a Luro-Jet® applicator guide, having a V-shaped slot which brings the array of extruded filaments together within

the slot and which includes an applicator at the base of the V-shape, which, in turn, includes an orifice through which the lubricant is pumped (metered) onto the yarn as it passes across the applicator.

- The extruder is a 1.5 inch (3.8 cm) diameter Hastelloy C-276 single screw extruder connected to a gear pump, which in turn is connected through an adapter to the spinneret assembly which includes a screen pack to filter the molten polymer. The spinneret assembly is the assembly 70 of Fig. 8 of the U.S. Patent Publication and includes a transfer line and spinneret faceplate depicted as elements 78 and 75, respectively, in Fig. 10. The spinneret faceplate has 30 holes arranged in a circle having a two-inch (5.1 cm) diameter, each hole (extrusion die orifice) has a diameter of 30 mils and a length of 90 mils. The annealer is that of Example 12 and Figs. 10A and 10B of the U.S. Patent Publication.

Operating temperatures are as follows:

- Extruder: 250°C, 265°C, 270°C at extruder zones - Feed, #1 and #2 respectively

Transfer line: 317°C

Spinneret faceplate: 350°C,

- Annealer: 204°C, 210°C, and 158°C at the #1, #2, and #3 positions, respectively.

The fluoropolymer throughput (fluoropolymer exiting the spinneret) is set by the gear pump to be the maximum, i.e., just short of causing melt fracture in the extruded filaments, this maximum being 50.5 g/min (6.7 lb/hr). The resultant yarn solidifies at a distance from the spinneret that is greater than 50X the diameter of the extrusion orifice. The lubricant described above is applied to the yarn just below the annealer and the feed rolls are at a temperature of approximately 180°C and surface speed of 309 m/min. The draw rolls are heated at 150°C and rotate at a surface speed of 1240 m/min to provide a draw ratio of 4.01. The yarn is wound onto a bobbin using a Leesona winder. The resultant yarn has the following properties: tenacity-3.45 gpd, elongation 7.7%, tensile modulus-55 gpd. When the draw ratio is decreased to 3.69 by reducing the surface speed of the draw rolls to 1140 m/min, the following yarn properties are obtained: tenacity-3.14 gpd, elongation-9.4%, modulus 51 gpd. The yarn denier increases from 374 to 407.

The coefficients of variation of the denier of the yarns is less than 2%. Coefficient of variation is the standard deviation divided by the mean weight of 5 consecutive ten meter lengths of the yarn (X 100).

Example 1

- The fluoropolymer yarn used in this Example is the yarn prepared generally by the process described above, except that the draw ratio is decreased slightly to obtain a higher elongation yarn having a lower tenacity. The yarn is 400 den, contains 13 filaments and has a tenacity of 2.9 gpd and elongation of 14.3%. The other yarn used in this Example is polyester yarn. One such yarn has 100 filaments, is 633 den after drawing (original denier 640) and has a tenacity of 7.89 gpd and elongation of 24% (PET Yarn A). PET Yarn A is dyed white and is obtained from the DuPont Company, Wilmington, DE). Another of such yarn has 108 filaments, is 885 denier after drawing and dyeing (original denier is 840), and has a tenacity of 7.49 gpd and elongation of 20% (PET Yarn B). PET Yarn B is an Akra Company yarn obtained from the United Yarn Co., Wayne, NJ, and is dyed a blue color.
- A yarn blend of the one end of the ETFE copolymer yarn and one end of PET Yarn A is made by air jet blending (co-mingling) as follows: A FOO entanglement machine is used. The machine uses an air interlace jet IMS type 3-2 obtained from the International Machinary Sales (IMS) inc., Winston-Salem, N.C. The fluoropolymer yarn is overfed through the jet at a yarn tension of 5 grams, the PET Yarn A is supplied through the jet at a yarn tension of 20 grams, the air pressure applied to co-mingle these yarns is 40 psi and the wind-up speed is 250 ypm. The resultant co-mingled yarn blend is a sheath/core yarn blend wherein the fluoropolymer yarn predominates at the surface of the yarn blend and has a denier of 1070, tenacity of 4.45 gpd and elongation of 21.83%.
- Another yarn blend is made by the same air jet co-mingling process, using the same ETFE copolymer yarn and PET Yarn B, one end of each yarn, to obtain a co-mingled sheath/core yarn blend having a denier of 1326, tenacity of 5.5 gpd, and elongation of 21.5%, and exhibiting a uniform blue color.
- Another yarn blend is made by the same air jet co-mingling process, using the two ends of the same ETFE copolymer yarn and one end of PET Yarn B, with both ETFE yarns being fed through the jet at the same tension, 5 g, and the PET Yarn tension being 20 g, to obtain a co-mingled yarn having a denier of 1728, tenacity of 3.93 gpd and elongation of 16.24%. The yarn blend of ETFE with PET Yarn A is white, and the yarn blend of ETFE with PET Yarn B is blue due to the use of a blue colored PET Yarn B.

Similar results are obtained when the PET yarns are replaced by polyamide or acrylic yarns.

Example 2

- Sewing thread of yarn is made of the co-mingled yarn prepared in
- 5 Example 1 using one end of the ETFE copolymer yarn and one end of PET Yarn B by (a) applying a twist to the yarn blend of one twist/cm, (b) plying three ends of such yarn together at a twist of one/cm but in the opposite direction from the twist in the yarn, and (c) heat setting the resultant thread at 140-150°C under tension. The resultant sewing thread
- 10 has a denier of 3978. A binder or finish can then be applied to the thread if desired. The resultant sewing thread is a balanced, corded construction having a uniform denier and exhibiting excellent stitch loop formation, without any propensity to knot or snarl.

Example 3

- 15 One end of 400 denier Kynar® 710 (PVDF yarn) and one end of 885 denier PET Yarn B are air-jet co-mingled together as described in Example 1 using the overfeed condition for the PVDF yarn, resulting in a blue colored yarn blend of 1290 denier, tenacity of 5.56 gpd, and elongation of 20.0%. The Kynar® 710 PVDF continuous filament yarn by itself has a tenacity of 3.1 gpd and 39.1% elongation.

Example 4

- One end of 885 denier PET Yarn B and one end of 20s/2 ply (512 denier) dark blue acrylic staple yarn and 1 one end of 400 denier ETFE
- 25 yarn are air-jet co-mingled as described in Example 3, with the ETFE and acrylic yarns both being overfed at the same tension, resulting in a tonal blue colored yarn blend of 1885 denier, tenacity of 3.97 gpd, and elongation of 20.5%. The 512 denier acrylic staple fiber is obtained through Pharr Yarns Inc., and has a tenacity of 1.7 gpd and elongation of 38.34%.

30 **Example 5**

- One end of 840 denier (840-140-400T), white high tenacity nylon from the DuPont Co. and one end of 400 denier ETFE are air-jet co-mingled as described in Example 3, resulting in a white yarn blend of 1263 denier, tenacity of 6.15 gpd, and elongation of 25.5%. The 840 denier
- 35 nylon filament yarn has a tenacity of 9.30 gpd, and elongation of 25.5%.

EXAMPLE 6

This Example describes the embodiment wherein the yarn blend contains binder for the second yarn, examples of such binder being

- polyurethane- or silicone- based polymer. These binders do not adhere to fluoropolymer but do serve to bind the composite yarn. The general procedure for applying binder (bonding agent) to yarn is to form a liquid medium containing the binder and apply it to the yarn by conventional
- 5 methods such as by using a kiss roll, padding of the binder medium onto the yarn or applying the medium to the yarn by dip or spray, followed by heat setting and wind-up on a final package.
- By way of example, commingled yarn is composed of one end of 400 denier, 13 dpf ETFE yarn and one end of 220 denier, 3.25 dpf
- 10 polyester yarn. The single yarn is characterized by 9S twist (9 turns/in (tpi), 9 turns/2.54 cm), i.e., 9 turns in the "S" direction. Two of these yarns are plied together, the plying being characterized by 7Z (7 tpi, 7 turns/2.54 cm), i.e., 7 turns in the "Z" direction. The binder is aqueous-based polyurethane available as NuBond® UVRH (Synthetic Thread, Bethlehem, PA) and is applied by a kiss roll to the plied yarn having a total measured denier of 1450, heat set and wound up on a final package. The resultant bound yarn performs better in industrial sewing by enabling the sewing to be carried out continuously for a much longer time than when the same yarn is used but without the binder. Thus, the use of the binder leads to
- 15 fewer yarn breaks or yarn entanglement, which are the typical causes for machine shutdown. This improved sewing performance is similar to the sewing performance for the polyester yarn used by itself together with the same binder. The binder effect on the polyester yarn by itself is similar to the effect of the binder on the composition EFTE/polyester yarn. Similar
- 20 improved sewing performance is obtained for a blend of the same yarns plied together to produce a composite yarn of 2572 measured denier to which the polyurethane binder is applied and heat set.

EXAMPLE 7

This Example is directed to the embodiment wherein the second

30 yarn weathers better when associated with the fluoropolymer yarn as a composite yarn, i.e., the strength deterioration of the second yarn is less in the yarn blend than when weathered as a yarn by itself, whereby the tensile strength of the yarn blend is higher than expected. This effect is obtained when the second yarn is polyester or polyamide. The yarns in

35 this Example are those described in Example 6.

Accelerated weathering performance is determined in accordance with SAE J1960 using a xenon arc accelerated weathering apparatus available from the Atlas Company, Chicago, Illinois. Tenacity and

- elongation of yarns are determined before and after exposure to 450 kilojoules energy (equivalent to more than four months outdoor exposure in Florida facing south at 45°). This exposure is enough to cause a 34% decrease in elongation of ETFE yarn by itself and a 63% decrease in
- 5 elongation of the polyester yarn by itself. In contrast, the decrease in elongation of the composite ETFE yarn/polyester yarn is only 37%, which is about the same as for the ETFE yarn by itself and which decrease is much less than the polyester yarn by itself. In addition, after the exposure, the tenacity (gpd) of the ETFE yarn by itself is almost
- 10 unaffected, while the polyester yan by itself retains only 43% of its original tenacity. In contrast, the composite yarn retains 91% of its original tenacity.

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